THE VERSATILITY OF ORGANOCLAY AND SURFACE-MODIFIED CLAY FOR REMEDIATION

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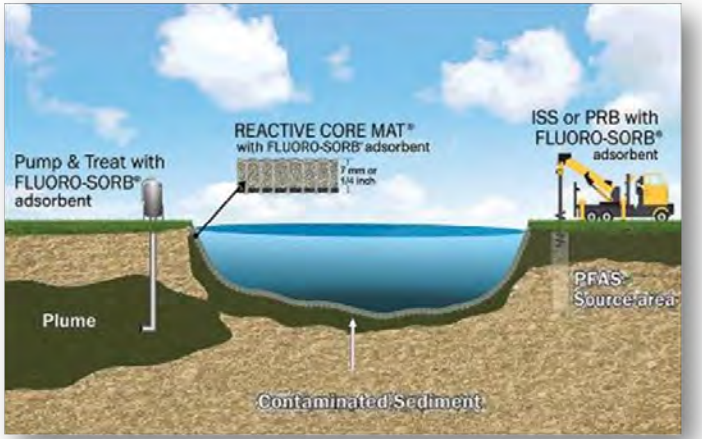
CETCO - Mineral Technologies Inc.

Missouri Waste Coalition Conference 2023



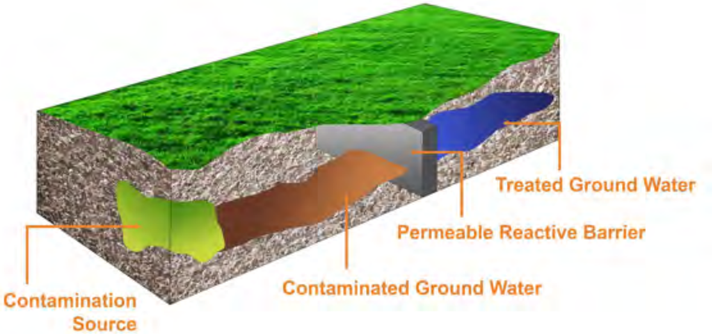
PRESENTATION OVERVIEW

1) Introduction to Surface Modified Clays (SMCs)
2) Organoclay Properties and Applications
3) PFAS Background
4) Introduction to Fluoro-Sorb
5) Summary of water/wastewater applications
6) ISS Applications
7) Reactive Core Mat (RCM) Applications
8) Injection Applications

MODIFIED CLAYS – VERSATILITY IN DEPLOYMENT

Source Zone Treatment
In Situ Stabilization/Solidification

Passive Groundwater
Permeable Reactive Barrier

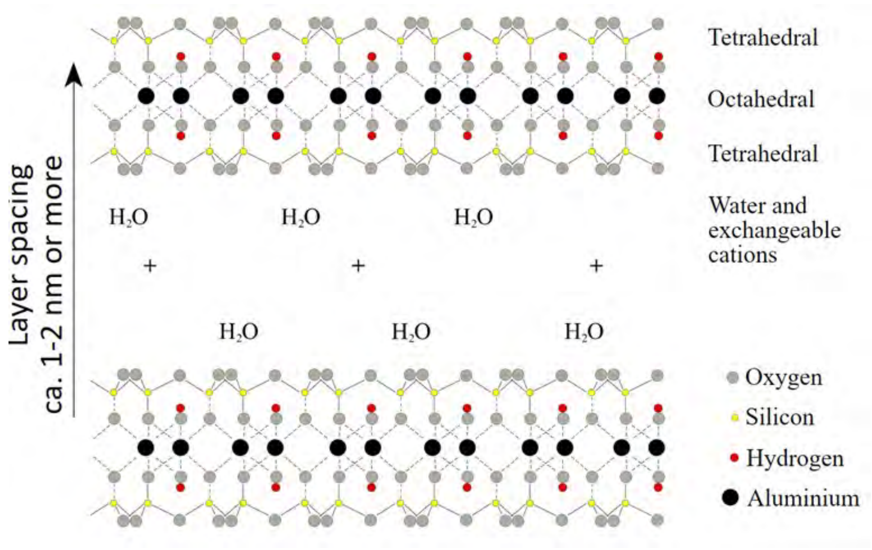


Water Filtration

Sediment Capping
REACTIVE CORE MAT® (RCM)

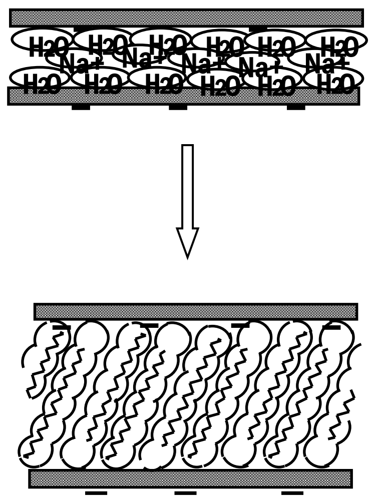
SODIUM BENTONITE CLAY

- Naturally-occurring mineral formed originally by natural weathering of volcanic ash when exposed to water
- Composed of at least 50% montmorillonite – 2 tetrahedral sheets of silica sandwich a central sheet of alumina (a 2:1 clay) – sheets are referred to as "platelets"
- A water-swelling clay that can form stable colloidal suspensions
- Water and exchangeable cations like sodium occupy the interlayer space
- Thickness of interlayer space plus one layer is called the d-spacing
- Typical d-spacing is 10 – 20 Å or 1-2 nm



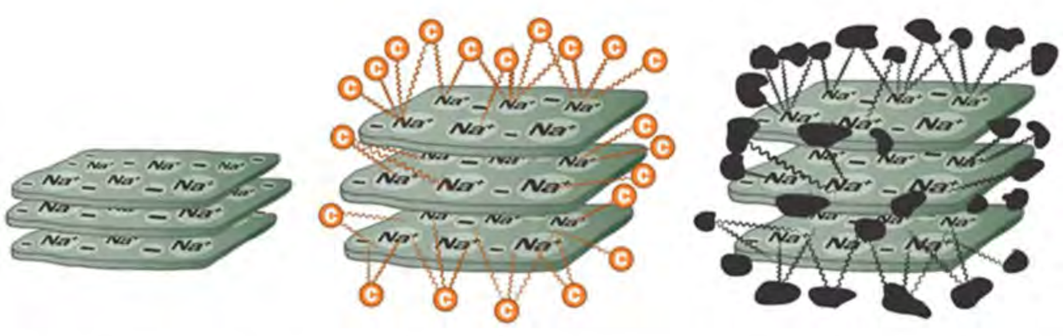
WHAT IS ORGANOCLAY?

Sodium Bentonite Clay



Organoclay

Organoclay is obtained by converting a hydrophilic clay to a hydrophobic clay using a surface modification agent through an ion-exchange reaction. Organoclay does not swell when hydrated.



Sodium Bentonite | Organoclay | Organoclay Saturated With Contaminants

Adsorption Mechanism

- Contaminant partitions to organoclay
- Extragallery and intragallery adsorption
- Primary driving forces are hydrophobic interactions between surface modification and contaminants.
- Secondary driving force hydrogen bonding with platelet edges have abundant hydroxyl groups.

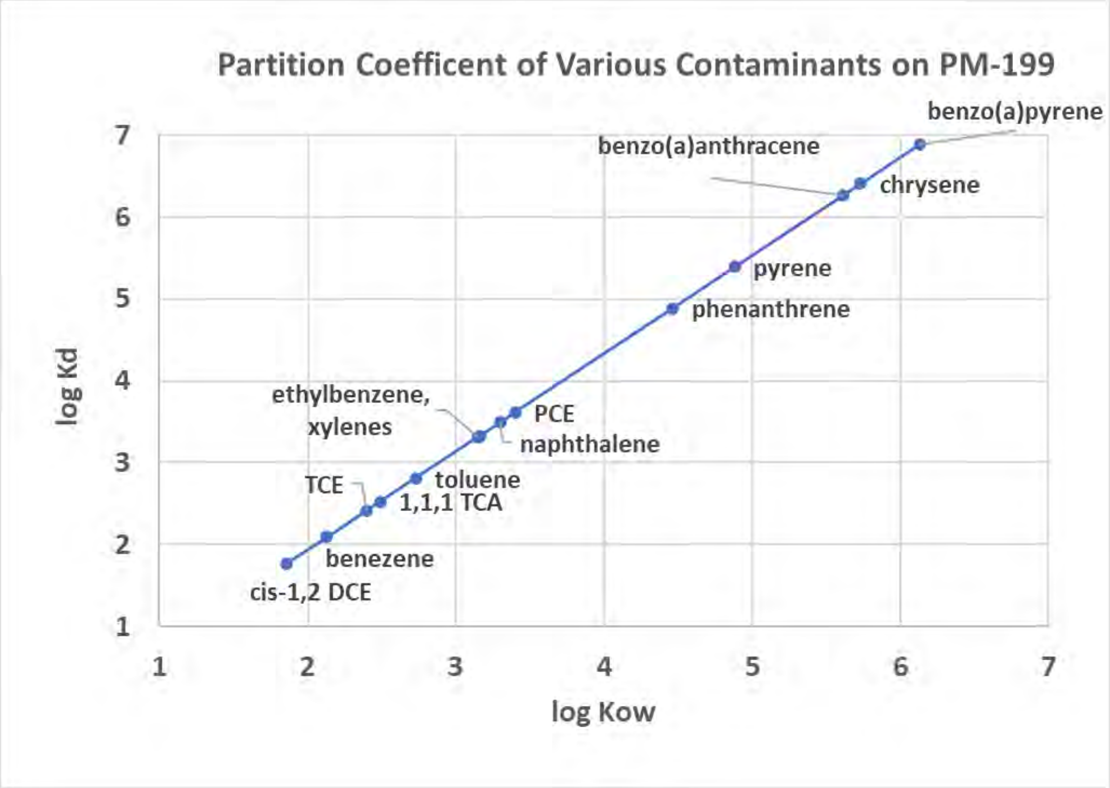
ORGANOCLAY PROPERTIES AND APPLICATIONS

- Dry, granular material
- Bulk Density: 50 lb/ft^3
- Specific Gravity: 1.75
- Contaminant Sorption Capacity:
  - Oil: 0.5 - 1.0 g/g organoclay (field)
  - LNAPL, DNAPL: 2 - 4 g/g organoclay (lab)

Product	Grain Size	Application
SS-199	Fine - 20x200 mesh	Soil Stabilization
PM-199	Standard - 18x40 mesh	Permeable Reactive Barriers Sediment caps Filtration Media
PM-200	Large - 12x30 mesh	Filtration Media Sediment Caps

ADSORPTION OF COMMON CONTAMINANTS

- Organoclay is a highly effective adsorption media for contaminants with low water solubility
- Partition coefficient is proportional to octanol-water partition coefficient



Compound	Solubility in water	Average Removal Amount
GRO, C6-C10	1 - 9.5 mg/L	95%
DRO, C10-C28	not soluble	100%
benzene	1750	20%
toluene	520	70%
ethylbenzene	170	95%
total xylenes	180	95%
naphthalene	31	95%
phenanthrene	1.2	95%
anthracene	0.04	95%
PCE	150	90%
TCE	1400	30%
cis-DCE	5000	0-5%

Reactive Core Mat® (RCM)

Variety of Media Used in RCM:

Fluoro-Sorb adsorbent - PFAS

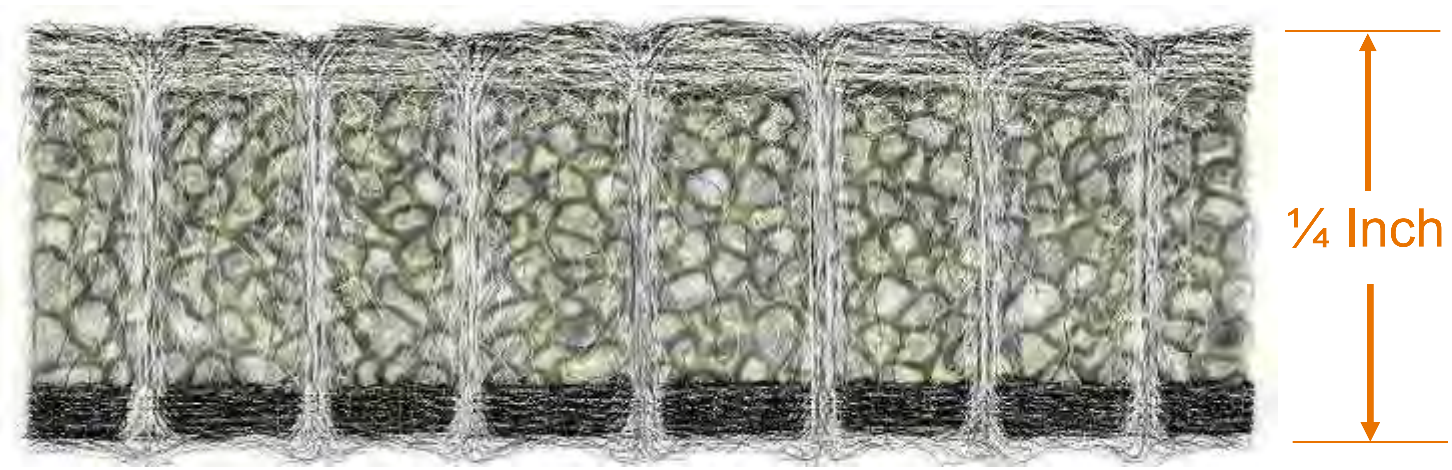
Organoclay for low soluble organic matter

Activated carbon soluble organics and some metals

Apatite minerals for heavy metals

Organoclay MRM media for Hg and Arsenic

Combinations of the above



Superfund Site, Portland, OR

Sediment Cap – Organic Bulk Deployment and RCM:

- NAPL from groundwater contaminating beach head and freshwater bay
- Gas releases carrying organic contaminants through water column and depositing on water surface
- A re-occurring sheen was developing on the surface of fresh water
- Sheen has completely dissipated in capped areas

PRE-REMEDIATION

POST-REMEDIATION

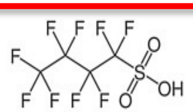
PFAS BACKGROUND

PFAS - Perfluoroalkyl & Polyfluoroalkyl Substances

- Thousands of PFAS were synthesized and manufactured for variety of uses
- Evolving recognition of which specific PFAS are contaminants of concern

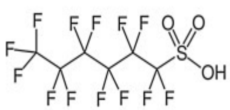
Perfluorosulfonic acid

C4



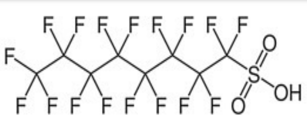
Perfluorobutane sulfonic acid (PFBS)

C6



Perfluorohexane sulfonic acid (PFHxS)

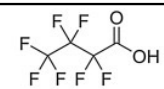
C8



Perfluorooctane sulfonic acid (PFOS)

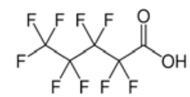
Perfluorocarboxylic acids

C4



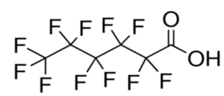
Perfluorobutanoic acid (PFBA)

C5



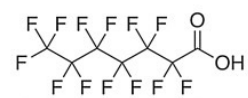
Perfluoropentanoic acid (PFPeA)

C6



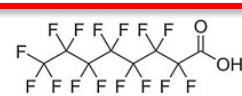
Perfluorohexanoic acid (PFHxA)

C7



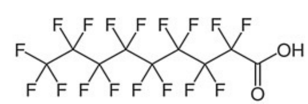
Perfluoroheptanoic acid (PFHpA)

C8



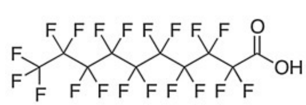
Perfluorooctanoic acid (PFOA)

C9



Perfluorononancanoic acid (PFNA)

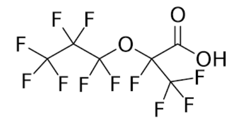
C10



Perfluorodecanoic acid (PFDA)

Gen X

C6



Hexafluoropropylene oxide dimer acid (HFPO-DA)

FLUORO-SORB® ADSORBENT FOR PFAS TREATMENT

- Proprietary surface-modified clay for the removal of PFAS from water or wastewater
- Commercially available since May 2019
  - ➢ Manufactured in ISO9001:2015 certified production plant in Aberdeen, Mississippi
  - ➢ Meets NSF/ANSI 61 Certification
- Partnerships with multiple universities for testing and engineering firms field piloting


FLUORO-SORB® 100


FLUORO-SORB® 200

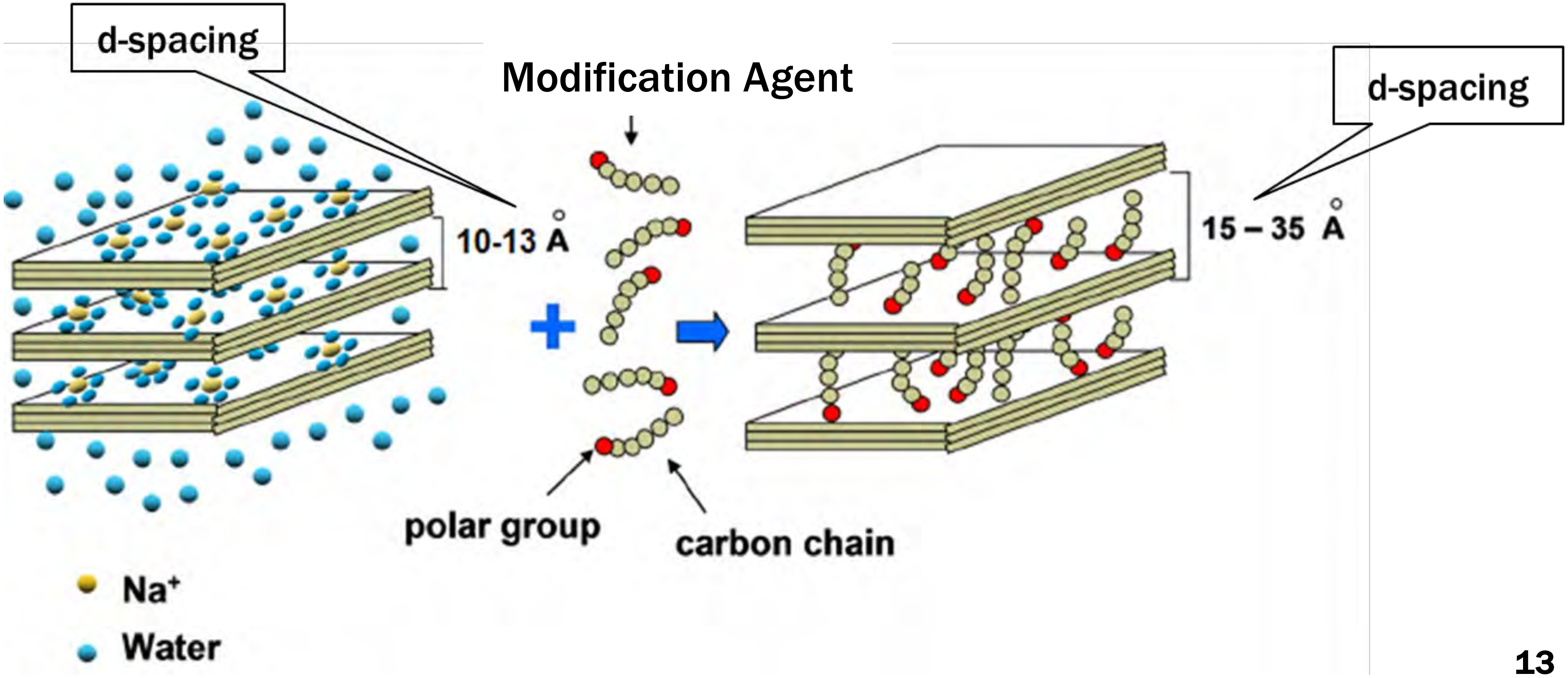

FLUORO-SORB® 300


FLUORO-SORB® 400

Certified to NSF/ANSI 61

FLUORO-SORB® ADSORPTION MECHANISM

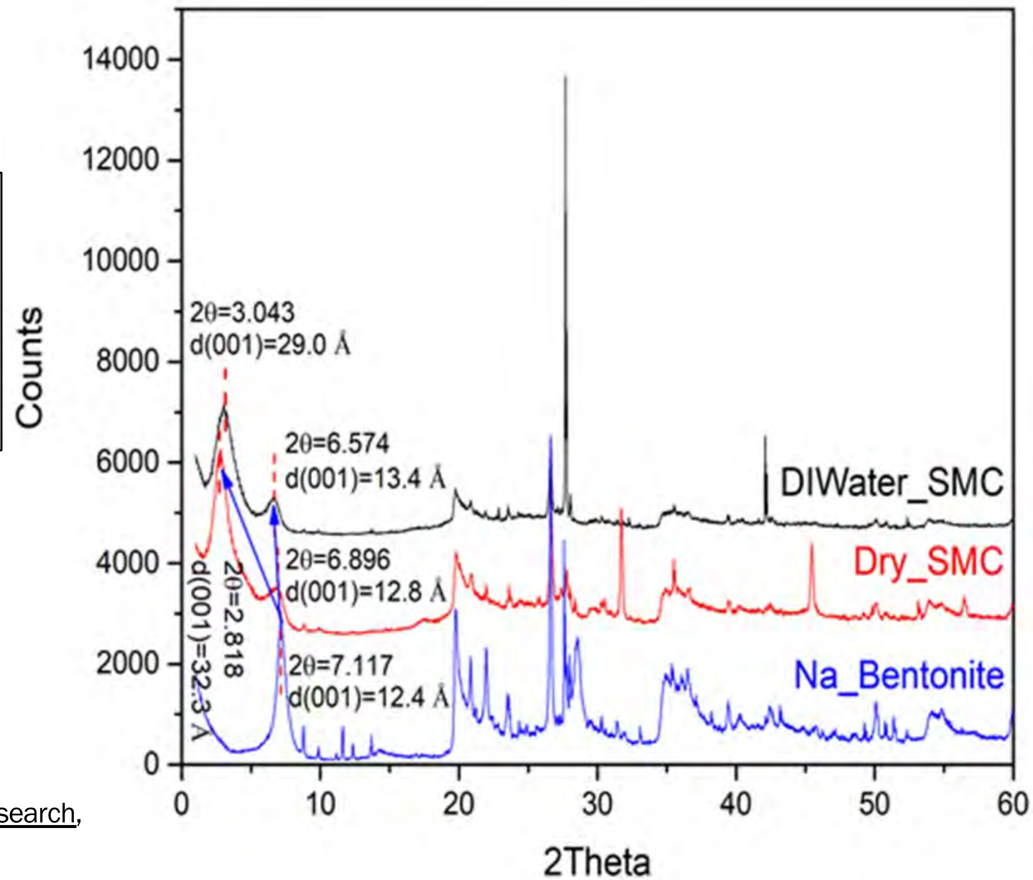
- Surface-modified clay adsorbents are obtained by converting a sodium bentonite clay to an adsorption media using a modification agent that has high affinity for a variety of PFAS
- The intralayer space or d-spacing increases as the modification agent bonds with the clay.
- PFAS are removed from water or stabilized in soil by adsorption – it is more energetically favorable for PFAS to partition into the adsorbent than remain in the water or soil.



WHAT IS SURFACE-MODIFIED CLAY?

- **Positively charged centers of modification agent attract anionic PFAS**
- **Hydrophobic chains of modification attract fluorinated chain of PFAS**
- **Loading of the modification agent renders the clay non-swellable upon hydration**

X-ray Diffraction (XRD) shows d-spacing increases:
- **12.4 Å for sodium bentonite**
- **29.0 - 32.3 Å for surface modified clay (SMC)**



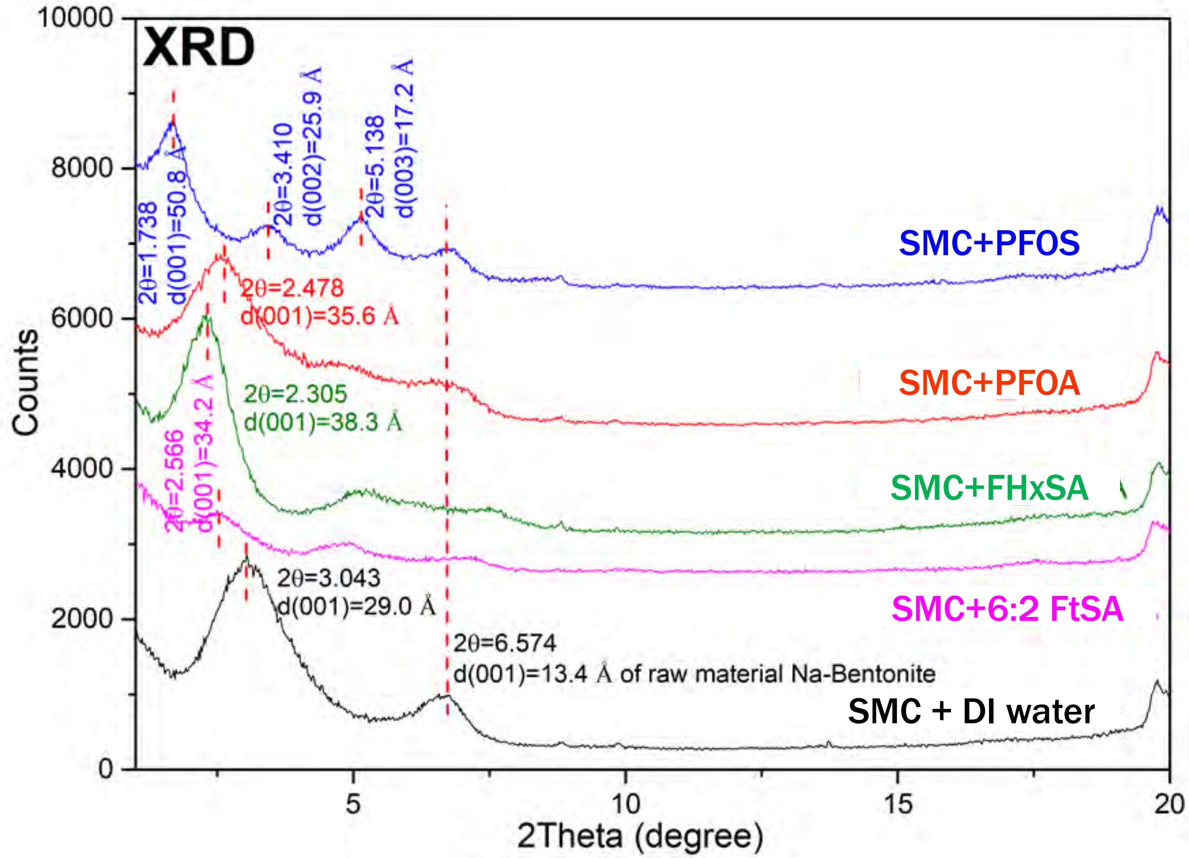
Yan, B., Munoz, G., Sauvé, S., and Liu, J. (2020) Water Research, 184, 116166.

PFAS ADSORPTION BEHAVIOR

XRD shows the d-spacing increases as PFAS are adsorbed

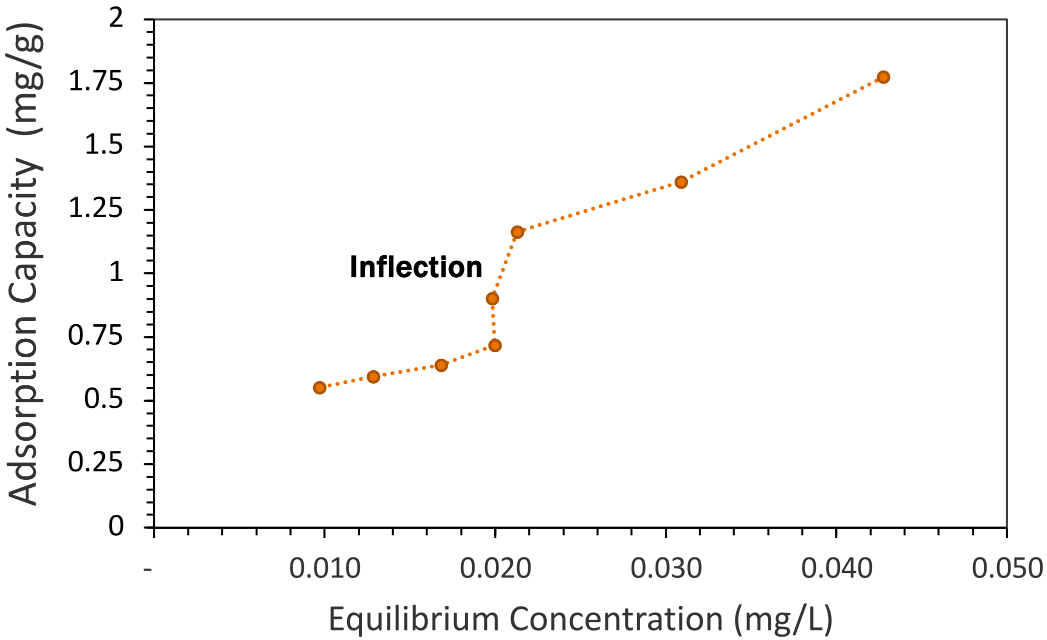
SMC = Surface-Modified Clay

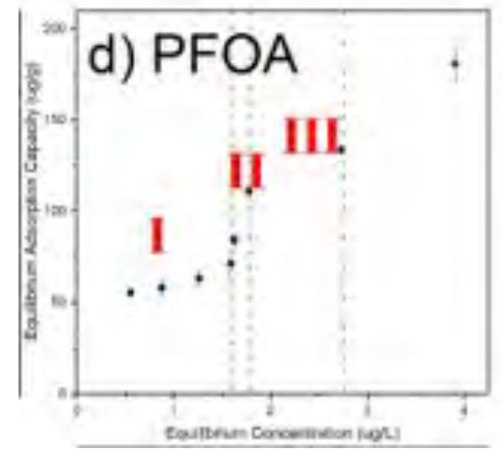
substance	d-spacing
SMC+DI water	29.0 Å
SMC+PFOS	50.8 Å
SMC+PFOA	35.6 Å
SMC+FHxSA	38.3 Å
SMC+6:2 FtSA	34.2 Å

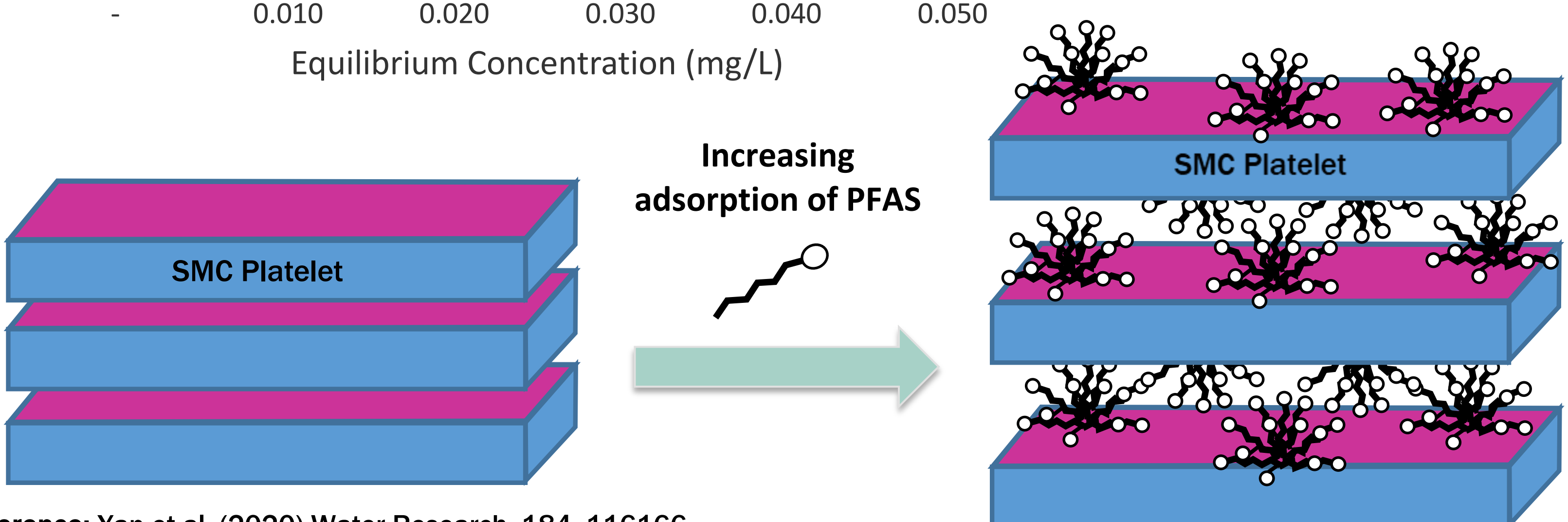


Yan, B., Wang, J., Liu, J. (2021) Water Research, 201, 117371.

SURFACE-MODIFIED CLAY (SMC) PFAS REMOVAL MECHANISM





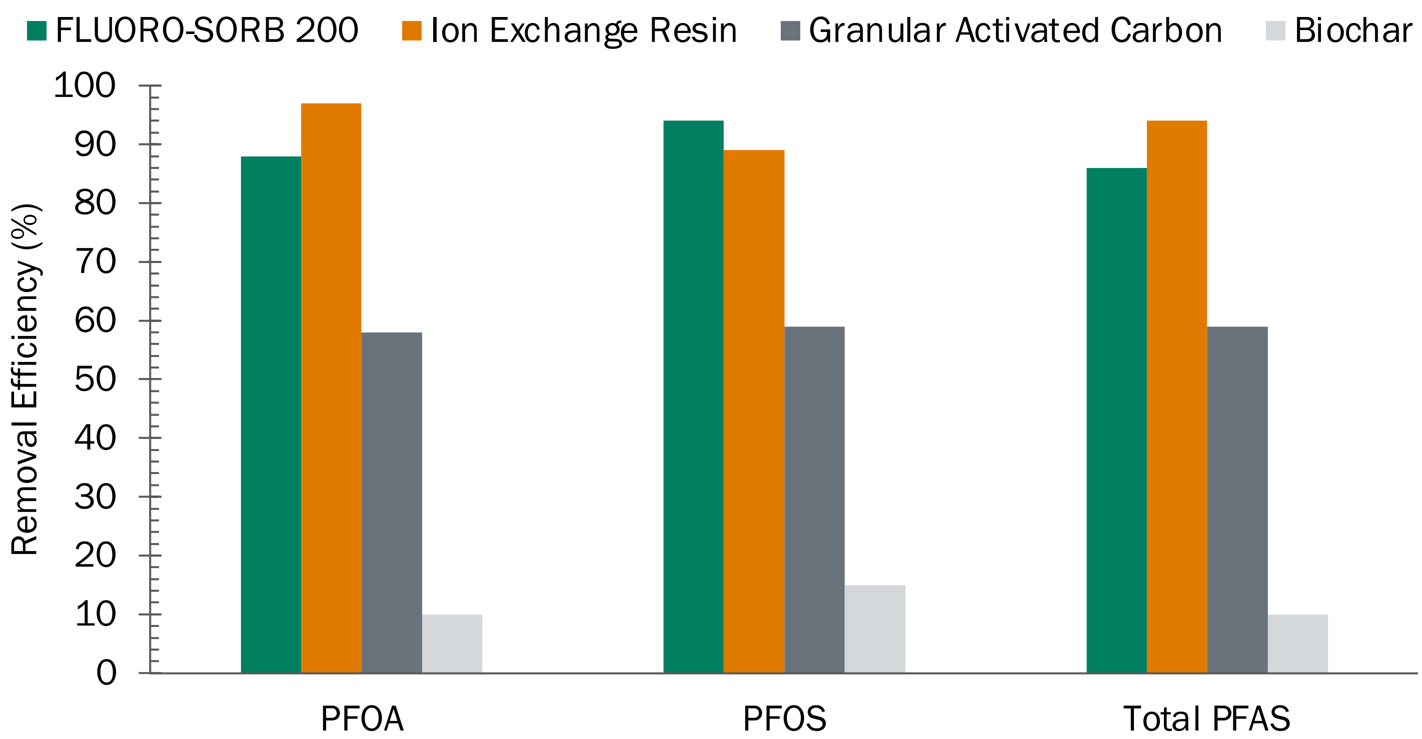


Reference: Yan et al. (2020) Water Research, 184, 116166

MINERALS TECHNOLOGIES CETCO

COMPARATIVE ASSESSMENT

- PFAS contaminated groundwater from a firefighting area at a former airfield
- Batch adsorption experiments - 40 mg FLUORO-SORB® adsorbent was mixed with 400 ml of contaminated groundwater for 168 hours and the supernatant analyzed for PFAS concentration



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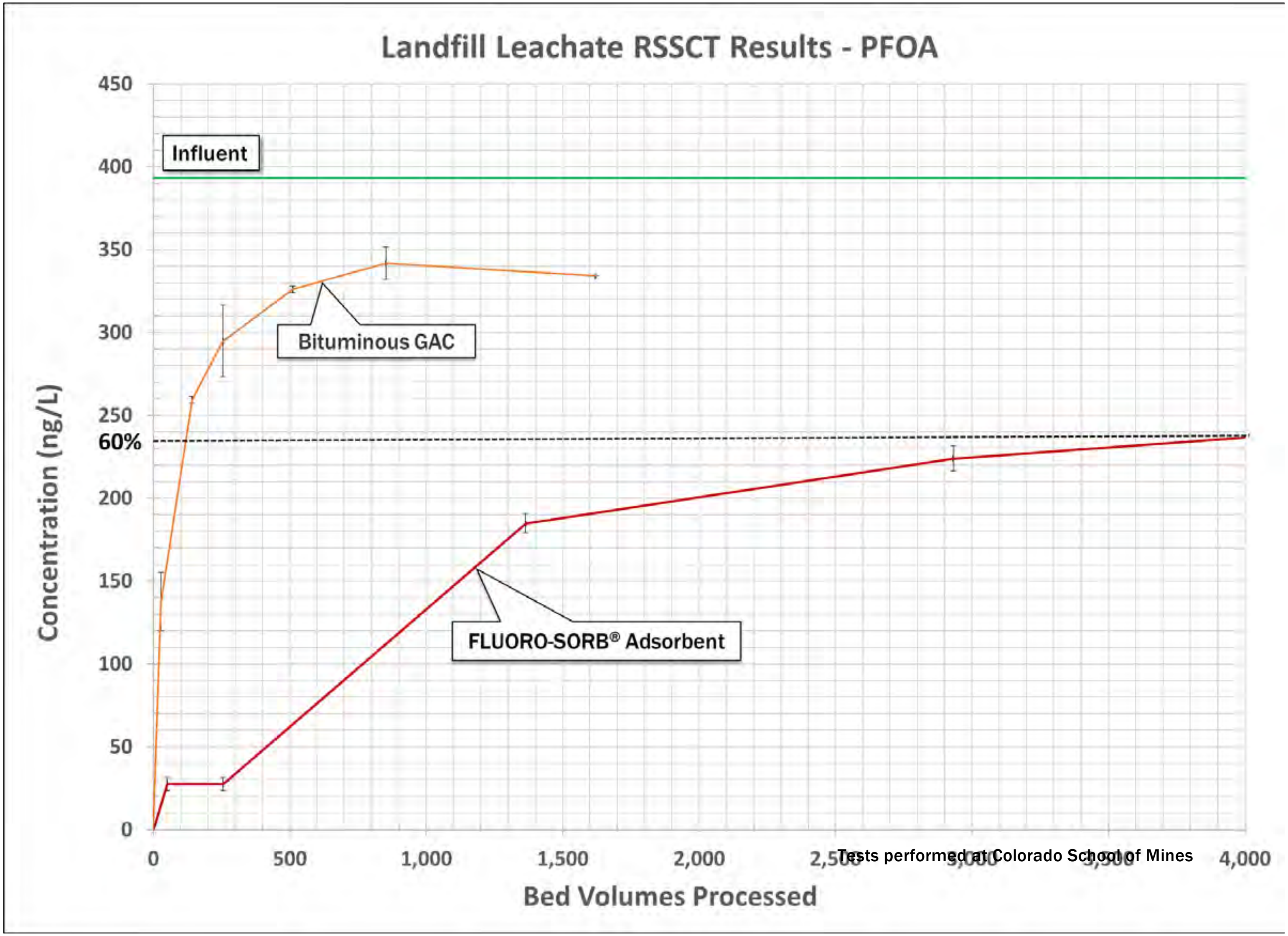
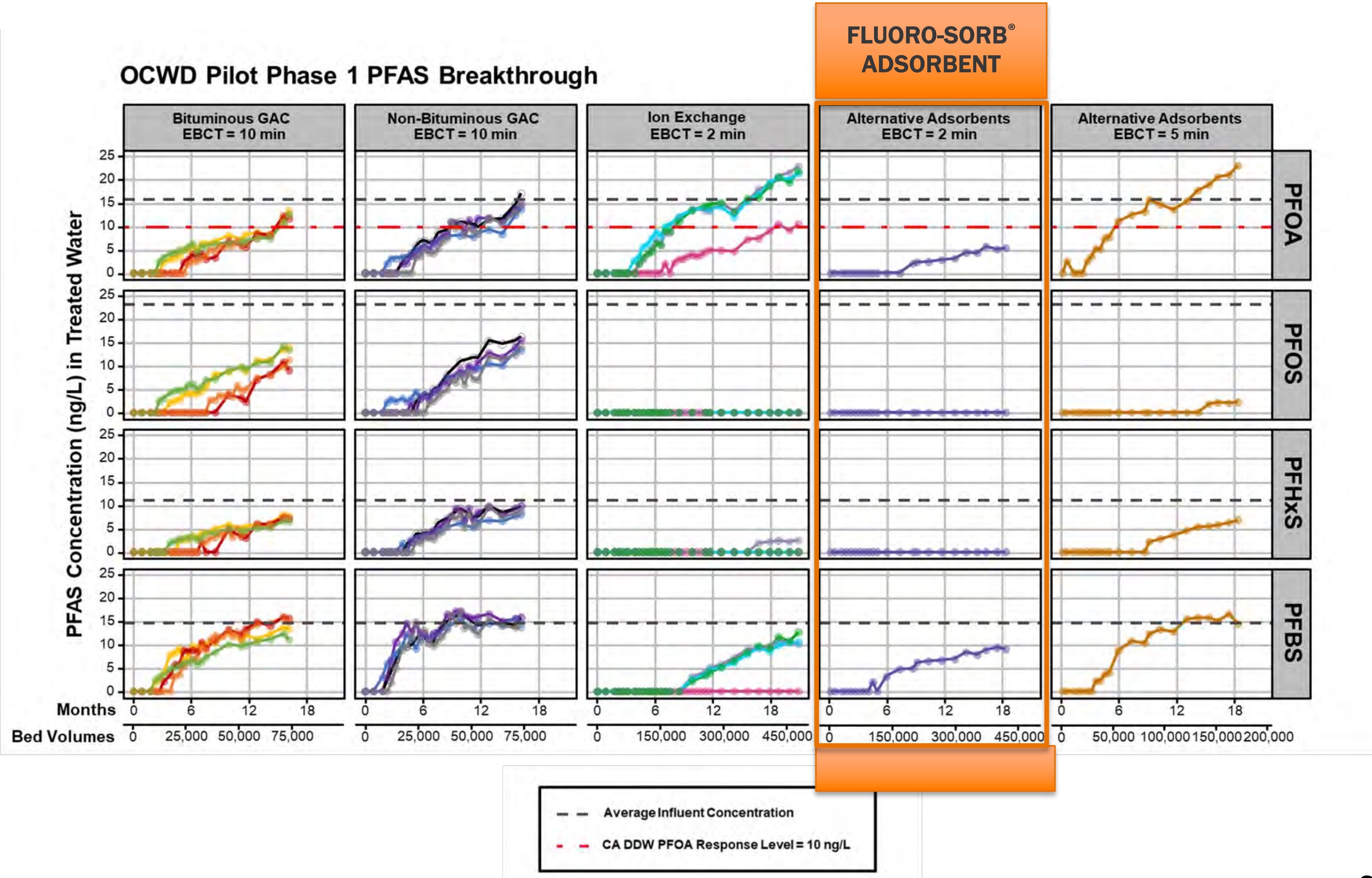


Landfill Leachate RSSCT Results - PFOA
Influent
Bituminous GAC
FLUORO-SORB® Adsorbent
60%
Concentration (ng/L)
Bed Volumes Processed
Tests performed at Colorado School of Mines
0
50
100
150
200
250
300
350
400
450
500
1,000
1,500
2,000
2,500
3,000
3,500
4,000

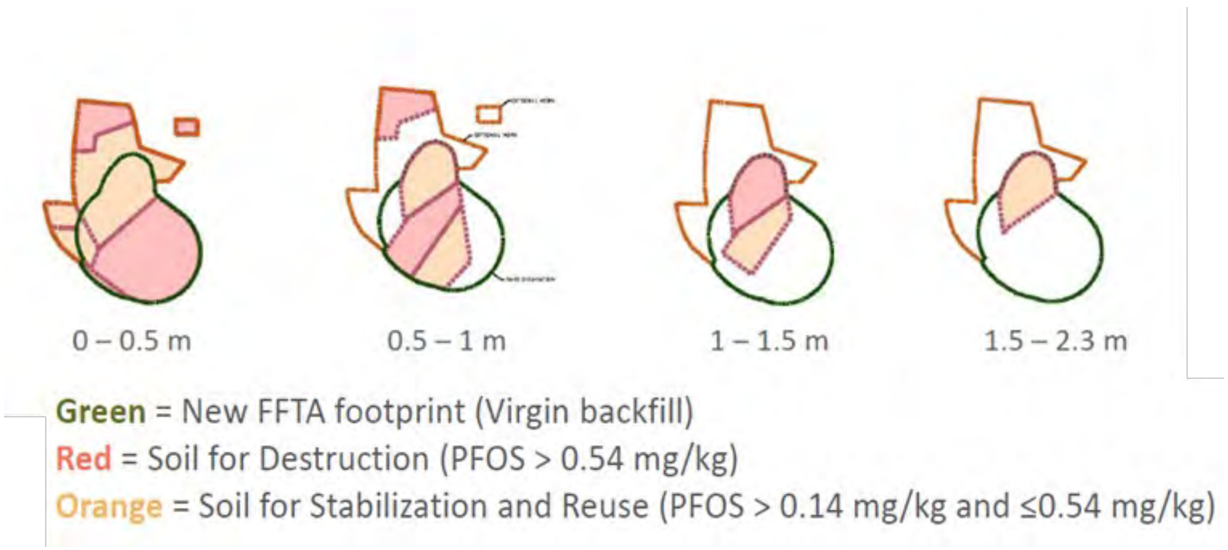
ONGOING PILOT RESULTS - OCTOBER 2021



Orange County Water District (2021). PFAS Phase 1 Pilot Scale Treatment Study Final Report. March 24, 2021

ISS FULL SCALE APPLICATION

- Fire fighting training area (FFTA) at a military site in Canada
- PFAS detected in soil and groundwater, with PFOS the main target of remediation
- Source zone treatment consisted of soil excavation (19,000 metric tons), with a portion of the excavated soil mixed with FLUORO-SORB® adsorbent to reduce PFAS leaching and backfilled into the excavation



Simplified vertical slices of the treatment zone. Zones are highlighted based on remediation approach (red zones – incineration, orange zones – soil stabilization with FLUORO-SORB adsorbent. The green area represents virgin backfill necessary for construction of a new fire training area.

IN SITU SOIL STABILIZATION (ISS) TREATABILITY STUDY

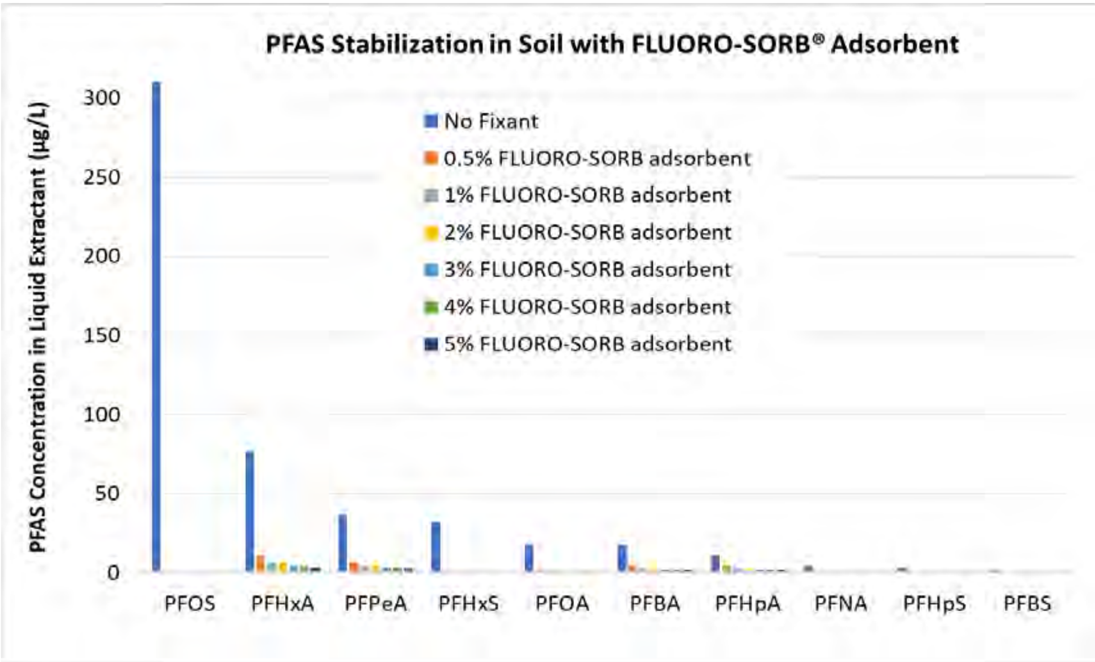
- Former fire fighting training area at a military installation
- In situ soil stabilization chosen as the remediation option for PFAS-impacted soil
- Bench-scale laboratory test completed to evaluate currently available commercial products as fixants for stabilization of PFAS in soil
- Representative soil samples were collected from the site
  - Sandy loam, with 94% ash content and 6% organic matter content
  - Samples were composited, and PFAS in soil was measured

<u>Procedure</u>

1. Composited soil (100 g) was mixed with 0.5% to 5% by weight of FLUORO-SORB® adsorbent and 200 mL of deionized water
2. Shaken for 120 hours and centrifuged to separate the liquid
3. Liquid analysed for PFAS concentrations

PFAS Name	Soil Concentration (µg/kg)	Compound Observed in Supernatent
Perfluorobutanoic acid (PFBA)	<10	Y
Perfluoropentanoic acid (PFPeA)	24.7	Y
Perfluorohexanoic acid (PFHxA)	22	Y
Perfluoroheptanoic acid (PFHpA)	<10	Y
Perfluorooctanoic acid (PFOA)	32	Y
Perfluorononanoic acid (PFNA)	15	Y
Perfluorobutanesulfonic acid (PFBS)	<10	Y
Perfluorohexanesulfonic acid(PFHxS)	80	Y
Perfluoroheptanesulfonic acid PFHpS	<10	Y
Perfluorooctanesulfonic acid (PFOS)	2933.3	Y
Perfluorooctane Sulfonamide (FOSA)	223.3	N
6:2 Fluorotelomer sulfonic acid	150	N
8:2 Fluorotelomer sulfonic acid	220	N

ISS LAB STUDY - RESULTS



PFAS	0.5% FLUORO-SORB Adsorbent	1% FLUORO-SORB Adsorbent	2% FLUORO-SORB Adsorbent	3% FLUORO-SORB Adsorbent	4% FLUORO-SORB Adsorbent	5% FLUORO-SORB Adsorbent
PFOS	99.8%	99.9%	100.0%	100.0%	100.0%	100.0%
PFHxA	85.6%	92.0%	92.0%	94.2%	94.1%	95.8%
PFPeA	82.5%	88.8%	88.5%	91.0%	90.7%	92.9%
PFHxS	99.1%	99.7%	99.9%	99.9%	99.9%	99.9%
PFOA	90.0%	92.8%	92.8%	94.8%	93.9%	96.1%
PFBA	76.0%	84.0%	84.6%	86.9%	86.9%	89.1%
PFHpA	60.0%	74.5%	72.7%	79.1%	78.2%	83.6%
PFNA	99.0%	99.0%	99.0%	99.0%	99.0%	99.0%
PFHpS	98.7%	98.7%	98.7%	98.7%	98.7%	98.7%
PFBS	97.8%	97.8%	97.8%	97.8%	97.8%	97.8%

ISS TREATABILITY STUDY - RESULTS

	Reduction in Leaching			
	PFOS		Average	
Fixant Weight %	FLUORO-SORB® Adsorbent	AlOH/GAC Fixant	FLUORO-SORB® Adsorbent	AlOH/GAC Fixant
0.5%	99.8%	54.8%	88.9%	46.3%
1%	99.9%	84.0%	92.7%	67.8%
2%	100.0%	94.2%	92.6%	80.2%
3%	100.0%	96.1%	94.1%	84.0%
4%	100.0%	98.3%	93.9%	89.0%
5%	100.0%	98.2%	95.3%	89.8%

Conclusion: For PFOS, the primary PFAS of concern at the site, leaching was reduced by 99.8% for the 0.5% by weight FLUORO-SORB adsorbent dose. In comparison, the 0.5% AlOH/GAC fixant reduced PFOS leaching by only 54.8%. It took 4-5% of the AlOH/GAC fixant to achieve the same reduction in leaching as 0.5–1% FLUORO-SORB adsorbent for the average of all PFAS tested.

PFAS SOLIDIFICATION/STABILIZATION

BENCH AND FIELD PILOT TESTING

Bench Testing

	Leach Fluid: DI Water at pH = 7.9					
Sample	Control 1 Soil/GW	Control 2 Soil/GW Cement	AIOH/ Carbon Blend	AIOH/Carbon Blend w/ Cement	FLUORO-SORB	FLUORO-SORB with Cement
PFAS Sum (mg/L)	228	1.17	0.75	245	0.30	0.04

Adapted from IN-SITU STABILIZATION OF PFAS IN GROUNDWATER, Peter Storch, Proceedings of Cleanup 2017 Melbourne, Victoria

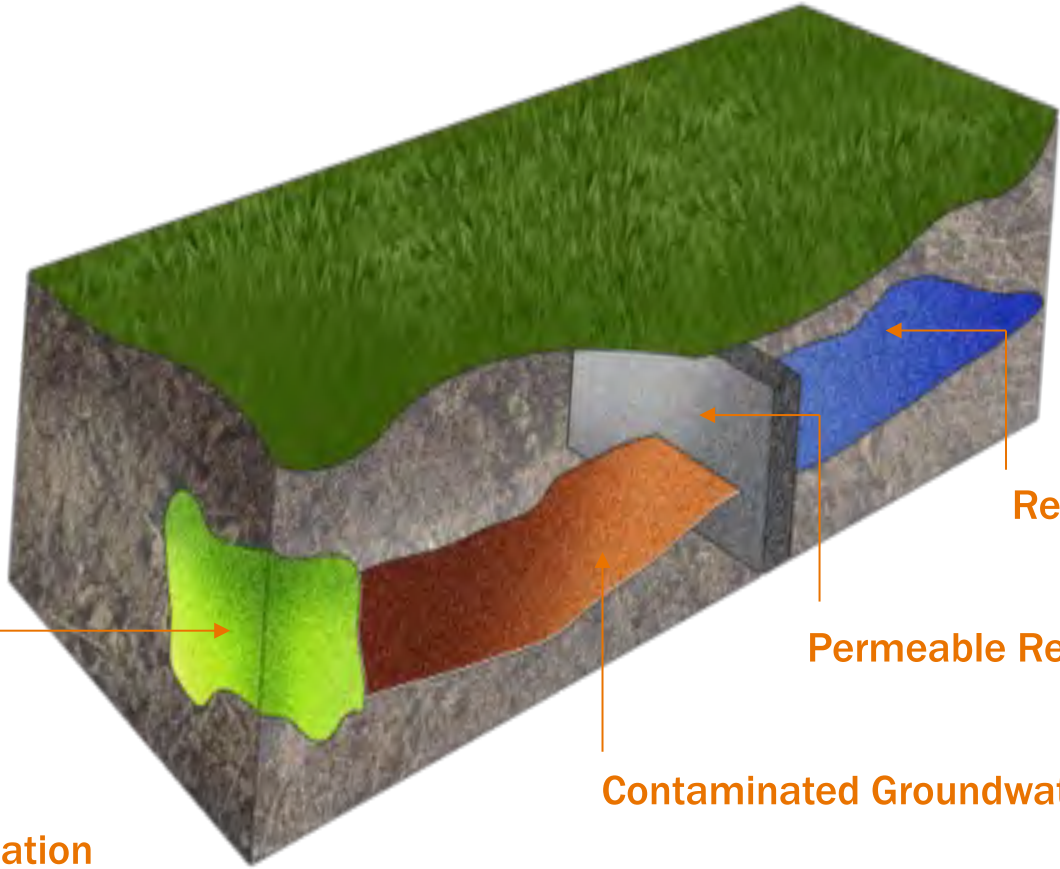
Field Pilot Testing

- Repeated bench testing, FLUORO-SORB® adsorbent selected for field pilot
- 5% FLUORO-SORB® adsorbent, 10% Portland Cement
- Installed in 2018
- Annual SPLP testing to verify long-term performance

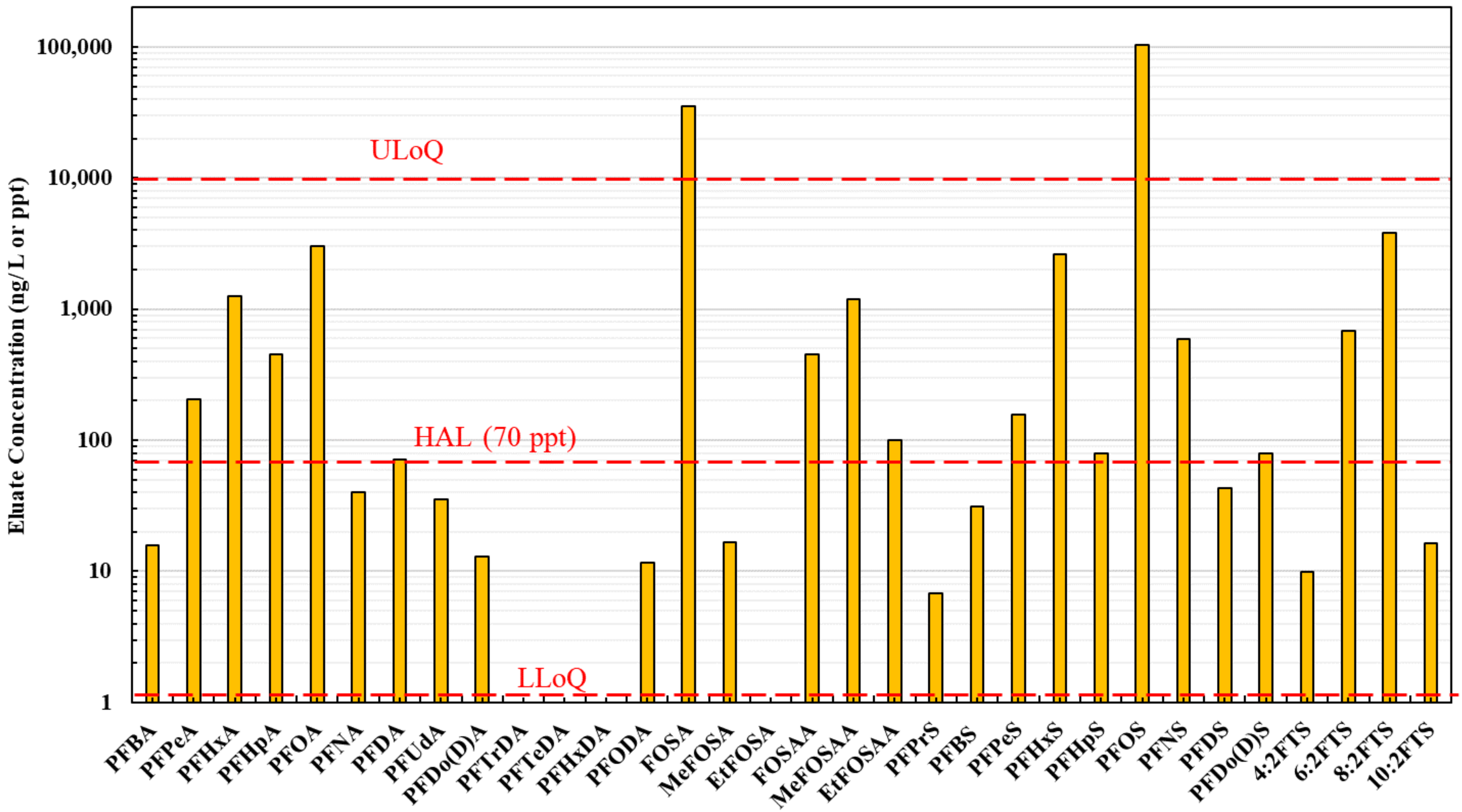
SOURCE ZONE TREATMENT & STABILIZATION

RESEARCH AT THE UNIVERSITY OF TEXAS

Pending Publication by Prof. Chadi El Mohtar and Antonios Alvertos, 2019

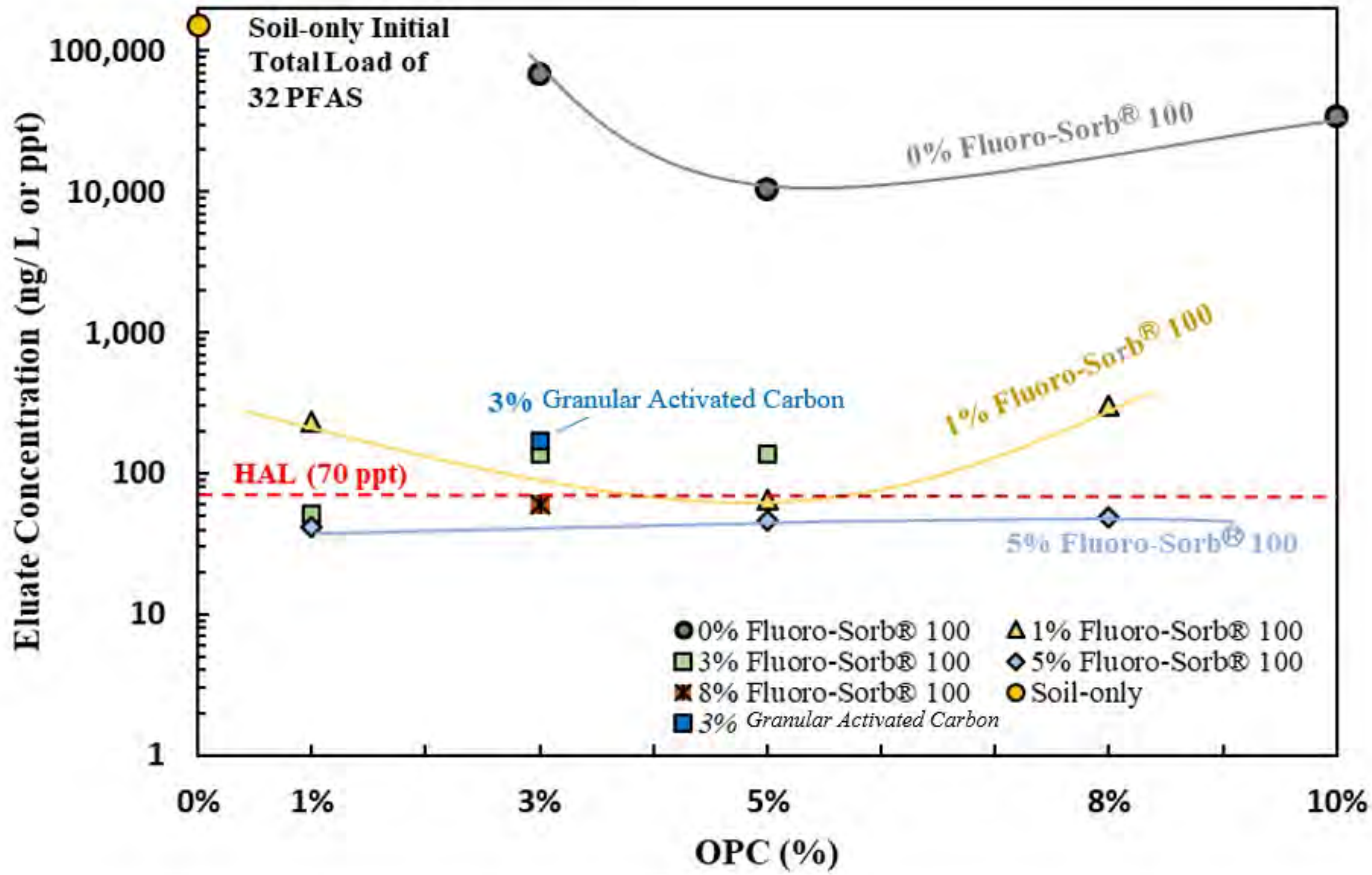


CHARACTERIZATION OF IN-SITU SOIL



US EPA LEAF METHOD 1313 & 1316

IMPACT OF FLUORO-SORB® 100 ADSORBENT & ORDINARY PORTLAND CEMENT

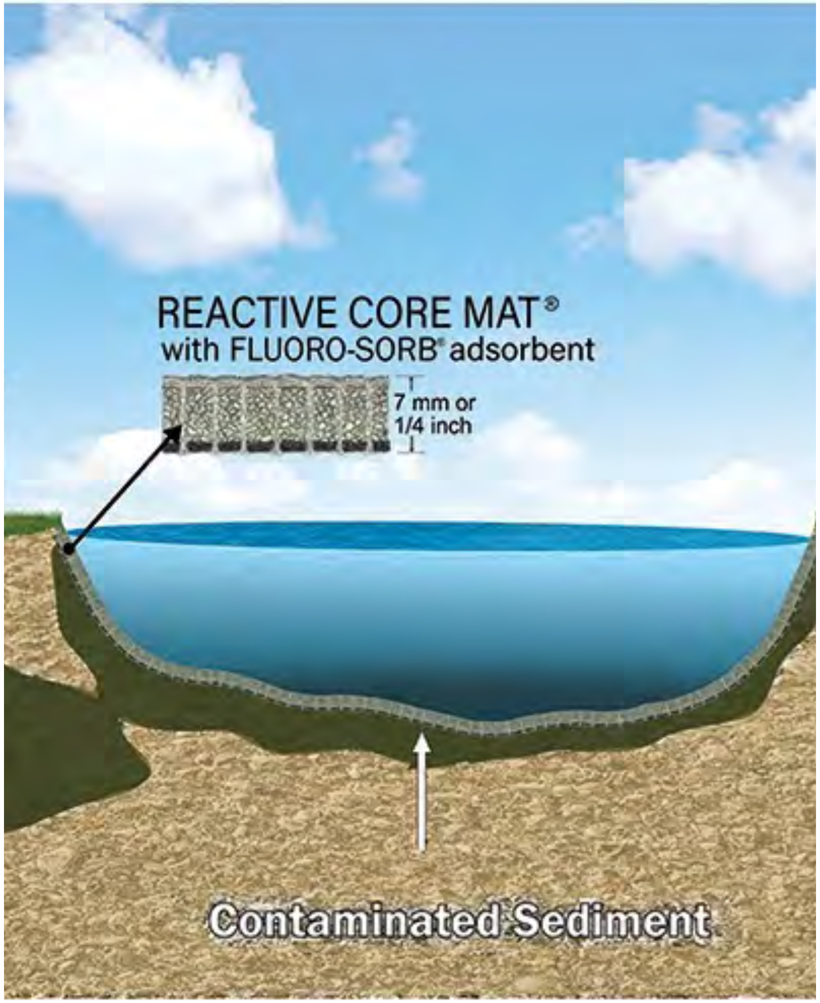


UNIVERSITY OF TEXAS CONCLUSIONS

USE OF FLUORO-SORB® ADSORBENT FOR SOURCE ZONE TREATMENT

1. OPC alone was not effective in stabilizing these same constituents
2. Mix III-F (5% OPC 5% FL) gave the optimal performance in terms of reducing total available PFAS for leaching (Method 1313) and the lowest mass transfer and transfer rate (Method 1315)

FLUORO-SORB® REACTIVE CORE MAT



INJECTION OF FLUORO-SORB

- CETCO has partnered with AST Environmental – For Insitu injection of Fluoro-Sorb for PRBs and Source Control
- Pilot Completed in 2022
- Several projects in the planning stage

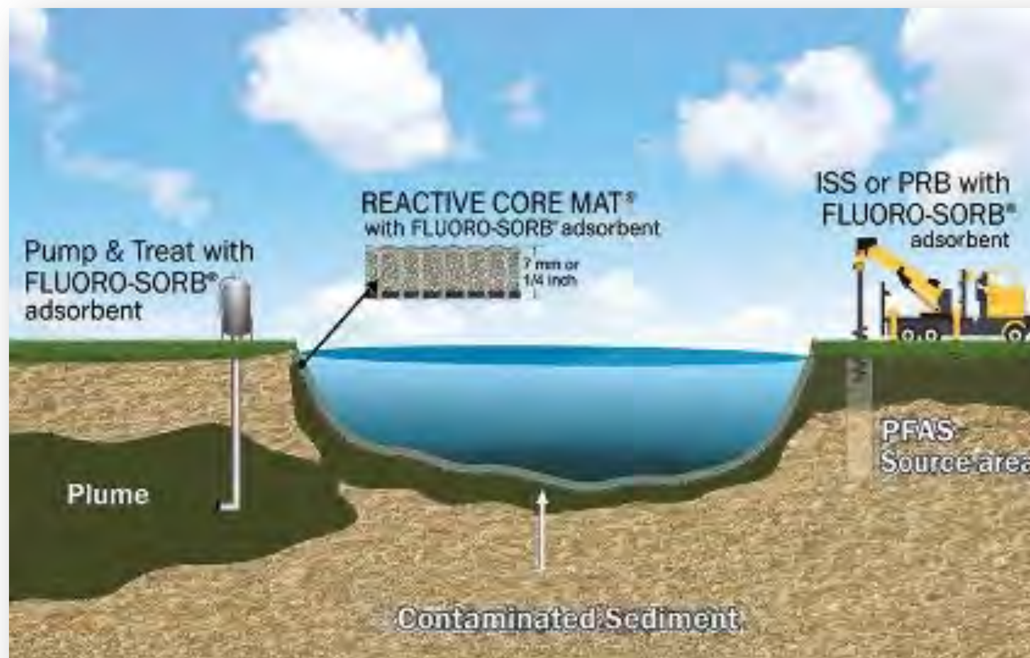
FLUORO-SORB® ADSORBENT – PILOT-SCALE INJECTION



CONCLUSIONS

Remediation with Organoclay and Surface-Modified Clay

- High adsorption capacity for a variety of contaminants
- Fast adsorption kinetics
- Resistant to competitive adsorption by co-contaminants and water constituents
- Versatility in deployment



Questions?

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OUR STANDARDS. YOUR PEACE OF MIND.

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